

# PATENT ABSTRACTS OF JAPAN

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(21)Application number : 2001-024261 (71)Applicant : ASAHI GLASS CO LTD

(22)Date of filing : 31.01.2001 (72)Inventor : ENDO EIJI

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## (54) GAS DIFFUSION ELECTRODE AND SOLID HIGH POLYMER TYPE FUEL CELL EQUIPPED WITH THIS

### (57)Abstract:

PROBLEM TO BE SOLVED: To provide a gas diffusion electrode having an outstanding electrode characteristic against oxygen reduction reaction, and a solid high polymer type fuel cell equipped with this, which can obtain high battery output.

SOLUTION: The gas diffusion electrode has a catalyst layer containing a catalyst and fluoride containing ion-exchange resin, and a gas diffusion layer arranged adjoining with the catalyst layer. A high molecular compound, which has an oxygen penetration coefficient of  $5 \times 10^{-11}$  [cm<sup>3</sup> (Normal).cm/cm<sup>2</sup>.s.Pa] or more, and does not have an ion exchange group substantially, is further contained in the catalyst layer.

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CLAIMS

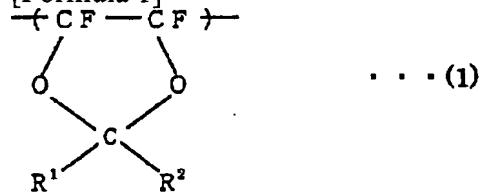
## [Claim(s)]

[Claim 1] The gas diffusion electrode which it is the gas diffusion electrode of porosity equipped with the catalyst bed containing a catalyst and fluorine-containing ion exchange resin, and an oxygen transmission coefficient is more than  $5 \times 10^{-11}$  [cm<sup>3</sup> (Normal), cm/cm<sup>2</sup>, and s-Pa] at said catalyst bed, and is characterized by containing further the high molecular compound which does not have an ion exchange group substantially.

[Claim 2] The gas diffusion electrode according to claim 1 characterized by being the polymer with which said high molecular compound includes the repeat unit based on the perfluorocarbon which has an aliphatic series ring structure.

[Claim 3] The gas diffusion electrode according to claim 2 characterized by expressing said repeat unit with the following type (1).

## [Formula 1]



[-- R1 and R2 show a fluorine atom or a trifluoromethyl radical independently among a formula (1), respectively.]

[Claim 4] The gas diffusion electrode according to claim 1 characterized by said high molecular compound being a polysiloxane compound.

[Claim 5] The gas diffusion electrode given in any of claims 1-4 they are with which content of said high molecular compound contained in said catalyst bed is characterized by being 0.01 to 30 mass % to the total amount of said catalyst and said fluorine-containing ion exchange resin.

[Claim 6] The polymer electrolyte fuel cell which is a polymer electrolyte fuel cell which has the polyelectrolyte film arranged between an anode, a cathode, and said anode and said cathode, and is characterized by having a gas diffusion electrode given in any of claims 1-5 they are as said cathode.

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**DETAILED DESCRIPTION**

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**[Detailed Description of the Invention]****[0001]**

[Field of the Invention] This invention relates to the polymer electrolyte fuel cell equipped with a gas diffusion electrode and this.

**[0002]**

[Description of the Prior Art] Since the formation of small lightweight is easy for the polymer electrolyte fuel cell which has the polyelectrolyte film, the utilization as migration cars, such as an electric vehicle, a power source of a small cogeneration system, etc. is expected. However, since operating temperature is comparatively low and the exhaust heat cannot use a polymer electrolyte fuel cell effectively for auxiliary machinery power etc. easily, for the utilization, the engine performance which can obtain high generating efficiency and high power density under the high actuation condition of the utilization factor of anode reaction gas (pure hydrogen etc.) and the utilization factor of cathode reaction gas (air etc.) is demanded.

[0003] The anode of a polymer electrolyte fuel cell and the electrode reaction in each catalyst bed of a cathode advance in the three-phase zone (henceforth a reaction site) to which each reactant gas, a catalyst, and fluorine-containing ion exchange resin (electrolyte) exist in coincidence. Therefore, in the polymer electrolyte fuel cell, conventionally, catalysts, such as a metal catalyst or metal support catalysts (for example, metal support carbon which supported metal catalysts, such as platinum, to carbon black support with a big specific surface area), are covered with the polyelectrolyte film, congener, or fluorine-containing ion exchange resin of a different kind, it is used as a component of a catalyst bed, and increase-ization of the reaction site concerned is attained by performing three-dimension-ization of the reaction site in the so-called catalyst bed.

[0004] The perfluorocarbon polymer (henceforth a sulfonic acid type perfluorocarbon polymer) with which ion conductivity which is represented by the "deflection myon" by Asahi Glass Co., Ltd. and "Nafion" by Du Pont etc. has a stable sulfonic group chemically under oxidization and reducing atmosphere highly as fluorine-containing ion exchange resin which covers the above-mentioned catalyst is used.

[0005] However, while excelling in ion conductivity and chemical stability, since the gas permeability in resin was inadequate, when using especially a gas diffusion electrode as a cathode, it was difficult [ the fluorine-containing ion exchange resin contained in the catalyst bed of the conventional gas diffusion electrode ] for the oxygen permeability in a catalyst bed to become inadequate, and for the overvoltage of the oxygen reduction reaction in a cathode to become large, and to acquire the high electrode characteristic.

[0006] On the other hand, in JP,11-354129,A, the solid-state macromolecule form fuel cell aiming at reduction of the overvoltage of a cathode is proposed by mixing a fluorine-containing ether compound to the fluorine-containing ion exchange resin which covers a catalyst, and making the oxygen permeability in the catalyst bed of a cathode increase to it.

**[0007]**

[Problem(s) to be Solved by the Invention] However, even if this invention persons were solid-state macromolecule form fuel cells given in JP,11-354129,A, the oxygen permeability in the catalyst bed of a cathode is inadequate, they cannot fully reduce the overvoltage of a cathode, and endurance of the catalyst bed of a cathode is inadequate, and they found out that there was a problem that a battery

life is short. Since the fluorine-containing ether compound made desirable is an oil-like low molecular weight compound, this dissolves in produced water gradually during a generation of electrical energy, or it accompanies to it, and this is desorbed from fluorine-containing ion exchange resin, and is further considered to be because for it to be discharged from a catalyst bed with generation water.

[0008] This invention is made in view of the technical problem which the above-mentioned conventional technique has, and aims at offering the polymer electrolyte fuel cell which can obtain the high cell output equipped with the gas diffusion electrode and this which have the outstanding electrode characteristic over an oxygen reduction reaction.

[0009]

[Means for Solving the Problem] this invention persons reached [ that the electrode characteristic in a cathode can be raised, and ] a header and this invention by making the catalyst bed of a cathode contain the high molecular compound which has high oxygen permeability and does not have an ion exchange group substantially, as a result of repeating research wholeheartedly in order to attain the above-mentioned purpose.

[0010] Then, it is the gas diffusion electrode of porosity equipped with the catalyst bed containing a catalyst and fluorine-containing ion exchange resin, and an oxygen transmission coefficient is more than  $5 \times 10^{-11}$  [cm<sup>3</sup> (Normal), cm/cm<sup>2</sup>, and s-Pa] at a catalyst bed, and this invention offers the gas diffusion electrode characterized by containing further the high molecular compound which does not have an ion exchange group substantially.

[0011] Since the high molecular compound (henceforth this high molecular compound) which has the above-mentioned oxygen transmission coefficient contains the gas diffusion electrode of this invention in the catalyst bed, it can make concentration of the reactant gas near [ in a catalyst bed ] the reaction site higher than before. Consequently, the exchange current density in electrode reaction can be increased, and an oxygen overvoltage can be reduced. That is, the high electrode characteristic can be acquired. If this gas diffusion electrode is especially used as a cathode of a polymer electrolyte fuel cell, since the overvoltage of the oxygen reduction reaction of a cathode can be reduced effectively, the electrode characteristic of a cathode can be raised.

[0012] moreover, the pore which has contributed to the gaseous diffusion in a catalyst bed since this high molecular compound contained in a catalyst bed functions also as a water repellent agent -- humidification -- service water and produced water can pile up and generating of the flooding by which pore will be blockaded can be prevented effectively. Furthermore, to aquosity solvents, such as water and alcohol, since this high molecular compound in this invention is substantially insoluble, it \*\*\*\*s near the catalyst during long-term actuation, and it can fully prevent generating of the fault of being discharged from a catalyst bed. Consequently, the gas diffusion electrode of this invention becomes possible [ it being stabilized and acquiring the high electrode characteristic over a long period of time, ].

[0013] Here, it becomes difficult to carry out highly enough concentration of the reactant gas near [ in a catalyst bed ] the reaction site to an oxygen transmission coefficient being under  $5 \times 10^{-11}$  [cm<sup>3</sup> (Normal), cm/cm<sup>2</sup>, and s-Pa], and it becomes difficult to fully reduce the overvoltage of an oxygen electrode reaction. Moreover, as for the oxygen transmission coefficient of this high molecular compound in this invention from the same viewpoint as the above, it is desirable that it is more than  $6 \times 10^{-11}$  [cm<sup>3</sup> (Normal), cm/cm<sup>2</sup>, and s-Pa].

[0014] In addition, the oxygen transmission coefficient of this high molecular compound in this invention sets in the demarcation membrane material gas transparency measuring device by the \*\*\*\*\* machine industrial company the cast film produced from this high molecular compound, and shows the oxygen transmission coefficient of the cast film in 25 degrees C measured based on the high vacuum method, and 105Pa.

[0015] Furthermore, "this high molecular compound which does not have an ion exchange group substantially" in this invention shows the high molecular compound whose ion exchange capacity in a molecule (henceforth AR) is below 0.10 milliequivalent / g desiccation resin (hereafter referred to as meq./g). To aquosity solvents, such as water and alcohol, since such this high molecular compound is substantially insoluble, it \*\*\*\*s near the catalyst during long-term actuation as mentioned above, and it can fully prevent generating of the fault of being discharged from a catalyst

bed. Moreover, as for AR of this high molecular compound of this, it is desirable that it is below 0.05meq./g from same viewpoint. Furthermore, ion exchange groups here are specifically a sulfonic group, a carboxylic-acid radical, etc.

[0016] Moreover, this invention is a polymer electrolyte fuel cell which has the polyelectrolyte film arranged between an anode, a cathode, and an anode and a cathode, and offers the polymer electrolyte fuel cell characterized by having the gas diffusion electrode of above-mentioned this invention as a cathode.

[0017] Thus, it becomes possible to constitute the polymer electrolyte fuel cell which has a high cell output by carrying out the cathode of the gas diffusion electrode of this invention which has the outstanding electrode characteristic over the oxygen reduction reaction described previously, and having it. Moreover, since it excels in endurance while the gas diffusion electrode of this invention can fully prevent generating of flooding as stated previously, the polymer electrolyte fuel cell of this invention equipped with this becomes possible [ it being stabilized and obtaining a high cell output over a long period of time, ].

[0018]

[Embodiment of the Invention] Hereafter, the suitable operation gestalt of the polymer electrolyte fuel cell equipped with the gas diffusion electrode of this invention and this is explained to a detail.

[0019] Although the cathode and anode which are the gas diffusion electrode of the polymer electrolyte fuel cell of this operation gestalt are equipped with a catalyst bed, it is desirable that all consist of a catalyst bed and a gaseous diffusion layer which adjoins this catalyst bed and is arranged. As a component of a gaseous diffusion layer, the porous body (for example, a carbon cross and carbon paper) which has electronic conduction nature is used, for example.

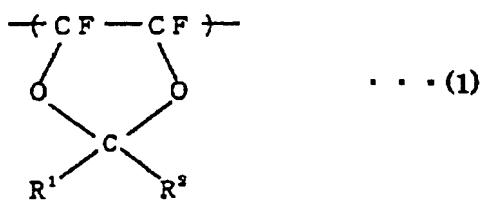
[0020] In the catalyst bed of a cathode, fluorine-containing ion exchange resin and this high molecular compound which the oxygen transmission coefficient which described it as the catalyst covered with this fluorine-containing ion exchange resin previously is more than  $5 \times 10^{-11}$  [cm<sup>3</sup> (Normal), cm/cm<sup>2</sup>, and s-Pa], and does not have an ion exchange group substantially mainly contain, and improvement in the electrode reaction rate of the cathode by reducing the overvoltage to the oxygen reduction reaction in a cathode is achieved.

[0021] Here, as for the weight average molecular weight of the viewpoint of supposing substantially that it is insoluble to aquosity solvents, such as water and alcohol, to this high molecular compound, it is desirable that it is 1000-3 million, and it is more desirable that it is 20000-1 million. In a long-term generation of electrical energy, it may drop out that the weight average molecular weight of this high molecular compound is less than 1000 of an electrode. On the other hand, if the weight average molecular weight of this high molecular compound exceeds 3 million, it will be hard coming to dissolve in a solvent, and the producing method will be restricted in the case of electrode production.

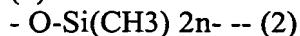
[0022] Moreover, as for this high molecular compound, it is desirable that it is a polymer including the repeat unit based on the perfluorocarbon which has an aliphatic series ring structure. It is hard to crystallize by torsion of the molecule resulting from the molecular structure, and a polymer including the repeat unit based on the perfluorocarbon which has an aliphatic series ring structure in intramolecular has high oxygen permeability. Moreover, it is meltable to a fluorine system solvent, and this polymer is excellent in chemical resistance, and since it is stability also in oxidation and reducing atmosphere, it is desirable.

[0023] As a repeat unit based on the perfluorocarbon which has the above-mentioned aliphatic series ring structure, the repeat unit expressed with the following type (1) is desirable. Here, R1 and R2 show a fluorine atom or a trifluoromethyl radical independently among the following type (1), respectively. As a compound which has such the molecular structure, "Teflon (trademark) AF 2400 etc." (oxygen transmission coefficient:  $1.2 \times 10^{-10}$  [cm<sup>3</sup> (Normal), cm/cm<sup>2</sup>, and s-Pa]) is mentioned as a trade name.

[Formula 2]



[0024] Moreover, when the compound which has different structure from the above-mentioned polymer as this high molecular compound is mentioned, as for this high molecular compound of this invention, it is desirable that it is a polysiloxane compound. Since a polysiloxane compound has high oxygen permeability, it is desirable. The poly dimethylsiloxane which has the repeat unit of the structure expressed with the following type (2) from a viewpoint of having the high oxygen transmission coefficient ( $6.95 \times 10^{-11}$  [cm<sup>3</sup> (Normal), cm/cm<sup>2</sup>, and s-Pa]) also in a polysiloxane compound is more desirable. Here, n shows the integer of 14 to  $4 \times 10^4$  among a formula (2).

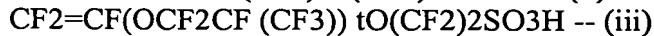
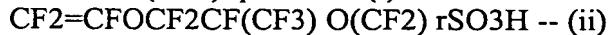
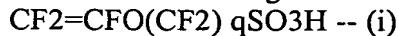


[0025] Moreover, as for the content of this high molecular compound contained in the catalyst bed, it is desirable that it is 0.01 to 30 mass % to the total amount of a catalyst and fluorine-containing ion exchange resin, and it is more desirable that it is 0.01 to 20 mass %. Here, the inclination it to become difficult to fully reduce an oxygen overvoltage [ as opposed to / that the content of this high molecular compound is under 0.01 mass % / an oxygen reduction reaction ] becomes large. On the other hand, if the content of this high molecular compound exceeds 30 mass %, in order that the reaction sites which the coverage of fluorine-containing ion exchange resin to the catalyst which the content of the fluorine-containing ion exchange resin contained in a catalyst bed falls relatively, consequently is contained in a catalyst bed falls, and function effectively may decrease in number, the inclination it to become difficult to acquire the high electrode characteristic becomes large.

[0026] Furthermore, although especially the catalyst included in the catalyst bed of the gas diffusion electrode of this invention is not limited, platinum or a platinum alloy is desirable. Furthermore, as for the catalyst contained in a catalyst bed, being supported by the support of electrical conductivity is desirable. Although especially this support is not limited, the carbon ingredient more than 200m<sup>2</sup>/g has a desirable specific surface area. For example, carbon black, activated carbon, etc. are used preferably.

[0027] Moreover, as for the fluorine-containing ion exchange resin contained in the catalyst bed of the gas diffusion electrode of this invention, it is desirable that it is a sulfonic acid type perfluorocarbon polymer. A sulfonic acid type perfluorocarbon polymer enables stable and prompt proton conduction chemically in a catalyst bed for a long period of time.

[0028] Furthermore, a sulfonic acid type perfluorocarbon polymer has the desirable copolymer which consists of a repeat unit (the integer of 1-12 and p of the integer of 0-3 and n is [ m ] 0 or 1 among a formula, and X is F or CF<sub>3</sub>) based on the fluoro vinyl compound expressed with CF<sub>2</sub>=CF-(OCF<sub>2</sub>CFX) m-Op-(CF<sub>2</sub>) n-SO<sub>3</sub>H, and a repeat unit based on tetrafluoroethylene. As a desirable example of the above-mentioned fluoro vinyl compound, the compound of (i) - (iii) is mentioned below. However, among the following type, in q, the integer of 1-8 and r show the integer of 1-8, and t shows the integer of 1-3.



[0029] In addition, as long as the repeat unit based on a fluorine-containing olefin or perfluoro (alkyl vinyl ether), such as hexafluoropropylene, is below 25 mass % of the repeat unit based on tetrafluoroethylene, it replaces the repeat unit based on tetrafluoroethylene, and may be included in the above-mentioned copolymer.

[0030] Moreover, as for AR of the fluorine-containing ion exchange resin contained in the catalyst bed of the gas diffusion electrode of this invention, it is desirable that it is 0.3-1.5meq./g. When AR of fluorine-containing ion exchange resin becomes under 0.3meq(s)/g, in order that reaction sites may decrease in number remarkably, there is an inclination it to become difficult to obtain sufficient cell output. On the other hand, if AR of fluorine-containing ion exchange resin exceeds 1.5meq(s)/g,

it will increase, the gaseous diffusion nature or wastewater nature in a catalyst bed will fall, and flooding will become easy to generate the consistency of the ion exchange group in fluorine-containing ion exchange resin. As for AR of the fluorine-containing ion exchange resin contained in the catalyst bed, it is more desirable from the same viewpoint as the above that it is 0.5-1.5meq./g. [0031] Moreover, if the thickness of the catalyst bed of the gas diffusion electrode of this invention is equivalent to the usual gas diffusion electrode, it is good, it is desirable that it is 1-100 micrometers, and it is more desirable that it is 3-50 micrometers.

[0032] In a polymer electrolyte fuel cell, since the overvoltage of the oxygen reduction reaction of a cathode is very large as compared with the overvoltage of the hydro acid-ized reaction of an anode, it is usually effective to make the oxygen density near [ in the catalyst bed of a cathode ] the reaction site increase as mentioned above, to use the reaction site concerned effectively, and to raise the electrode characteristic of a cathode, when raising the output characteristics of a cell.

[0033] On the other hand, although especially the configuration of an anode is not limited, for example, you may have the configuration of a well-known gas diffusion electrode, it is desirable to constitute so that it may have the same structure as the above-mentioned cathode. Also when becoming possible to also raise the electrode characteristic of an anode by this in addition to a cathode, and raising a cell output more and performing actuation over a long period of time, it can plan holding the high cell output more certainly.

[0034] Moreover, the polyelectrolyte film used for the polymer electrolyte fuel cell of this invention will not be limited especially if it is the ion exchange membrane which shows good ion conductivity under a damp or wet condition. The perfluorocarbon polymer which has the perfluorocarbon polymer which has a sulfonic group, polysulphone resin, a phosphonic acid radical, or a carboxylic-acid radical as solid-state polymeric materials which constitute the polyelectrolyte film, for example can be used. Especially, a sulfonic acid type perfluorocarbon polymer is desirable. And this polyelectrolyte film may consist of the same resin as the fluorine-containing ion exchange resin contained in a catalyst bed, and may consist of different resin.

[0035] As for the gas diffusion electrode of this invention, it is desirable that fluorine-containing ion exchange resin, a catalyst, and this high molecular compound produce using the coating liquid dissolved or distributed to a solvent or a dispersion medium. As the solvent used here or a dispersion medium, alcohol, fluorine-containing alcohol, the fluorine-containing ether, etc. can be used, for example. And a catalyst bed is formed by carrying out coating of the coating liquid to the carbon cross used as an ion exchange membrane or a gaseous diffusion layer etc. Moreover, coating of the above-mentioned coating liquid is carried out to the base material prepared separately, a coating layer is formed, and a catalyst bed can be formed on ion exchange membrane also by imprinting this on ion exchange membrane.

[0036] Here, when a catalyst bed is formed on a gaseous diffusion layer, it is desirable to join a catalyst bed and ion exchange membrane with the pasting-up method (JP,7-220741,A, JP,7-254420,A), a hotpress, etc. Moreover, although a gas diffusion electrode may be constituted only from a catalyst bed when a catalyst bed is formed on ion exchange membrane, a catalyst bed is adjoined further, a gaseous diffusion layer is arranged, and it is good also as a gas diffusion electrode.

[0037] The separator with which the passage of gas was usually formed is arranged, the gas which contains hydrogen in an anode in the passage concerned, and the gas which contains oxygen in a cathode are supplied to the outside of a gas diffusion electrode, and a polymer electrolyte fuel cell is constituted.

[0038]

[Example] Although an example and the example of a comparison are given and the gas diffusion electrode and polymer electrolyte fuel cell of this invention are explained in detail hereafter, this invention is not limited to these examples.

[0039] (Example 1) The unit cell of an example 1 was produced with the procedure explained below. The catalyst used for carbon black powder what did 40 mass % support of platinum. Using the fluorine-containing ion exchange resin (it is called fluorine-containing-ion-exchange-resin A AR=0.91meq./g and the following) which consists of a copolymer which consists of a repeat unit based on tetrafluoroethylene, and a repeat unit based on  $\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_3\text{H}$  as

fluorine-containing ion exchange resin, it was made to dissolve in ethanol and the ethanol solution whose concentration of this fluorine-containing ion exchange resin is 5 mass % was prepared. Moreover, the Du Pont trade name "Teflon AF 2400" was prepared as this high molecular compound, this was dissolved in the perfluoro OKUTA decane and the perfluoro OKUTA decane solution whose concentration of this Teflon AF 2400 is 1 mass % was prepared. Next, an ethanol solution, an above-mentioned perfluoro OKUTA decane solution, and an above-mentioned catalyst were mixed, and the catalyst dispersion liquid C1 for catalyst bed formation of a cathode were prepared. In addition, the mass ratio of the catalyst in these catalyst dispersion liquid C1 (the mass of support is included), fluorine-containing ion exchange resin, and this high molecular compound was set to mass =0.8:0.15:0.05 of the mass:book high molecular compound of mass:fluorine-containing ion exchange resin of a catalyst.

[0040] Moreover, the above-mentioned fluorine-containing-ion-exchange-resin A was dissolved in ethanol, and the ethanol solution was prepared. Next, it added in the above-mentioned ethanol solution, the powder of the same catalyst as what was used by catalyst dispersion liquid C1 was fully mixed, and the catalyst dispersion liquid A1 for catalyst bed formation of an anode were prepared. In addition, the catalyst in these catalyst dispersion liquid A1 (the mass of support is included) and the mass ratio of fluorine-containing ion exchange resin were set to mass =0.8:0.2 [ of a catalyst ] of mass:fluorine-containing ion exchange resin.

[0041] Next, the thing with a thickness of 300 micrometers which carried out the weather strip of the water-repellent carbon cross (fiber textile fabrics) in the water-repellent carbon powder layer (mixture of carbon black and PTFE) was prepared as a gaseous diffusion layer. Moreover, the ion exchange membrane (trade name: the deflection myon S, the Asahi Glass Co., Ltd. make, AR=1.0meq./g, 80 micrometers of desiccation thickness) which consists of a sulfonic acid type perfluorocarbon polymer was prepared as polyelectrolyte film.

[0042] Next, catalyst dispersion liquid 1 were sprayed on one field of the above-mentioned polyelectrolyte film so that the content of the platinum of the catalyst bed of a cathode might serve as 0.5 mg/cm<sup>2</sup>. Moreover, catalyst dispersion liquid A1 were sprayed on another field of the above-mentioned polyelectrolyte film so that the content of the platinum of the catalyst bed of an anode might serve as 0.5 mg/cm<sup>2</sup>. Next, the polyelectrolyte film which sprayed above-mentioned catalyst dispersion liquid C1 and above-mentioned catalyst dispersion liquid A1 was dried at 100 degrees C among atmospheric air for 1 hour.

[0043] Moreover, the perfluoro OKUTA decane solution whose concentration of above-mentioned Teflon AF 2400 is 5 mass % was slushed into the petri dish, the solvent was removed after that and the cast film of Teflon AF 2400 whose thickness is 90 micrometers was produced. Furthermore, the ethanol solution whose concentration of the above-mentioned fluorine-containing ion exchange resin is 5 mass % was slushed into the petri dish, and the cast film of the fluorine-containing ion exchange resin whose thickness is 90 micrometers was produced. And the oxygen transmission coefficient of the cast film of Teflon AF 2400 and the cast film of fluorine-containing ion exchange resin was measured by the conditions and approach which were previously described using the demarcation membrane material gas transparency measuring device by the \*\*\*\*\* machine industrial company. Consequently, the oxygen transmission coefficient of the cast film of Teflon AF 2400 was 1.2x10-10 [cm<sup>3</sup> (Normal), cm/cm<sup>2</sup>, and s-Pa], and the oxygen transmission coefficient of the cast film of fluorine-containing ion exchange resin was 4.8x10-12 [cm<sup>3</sup> (Normal), cm/cm<sup>2</sup>, and s-Pa].

[0044] (Example 2) Instead of the perfluoro OKUTA decane solution of Teflon AF 2400 prepared in the example 1 Dissolve the trade name "dimethyl silicone (KF96H -1 million)" by Shin-Etsu Chemical Co., Ltd. in toluene as this high molecular compound, and the toluene solution the concentration of whose is 5 mass % is prepared. Except having used this, catalyst dispersion liquid C2 were prepared like the example 1, and the electrode and the film zygote were produced like the example 1 except having produced the cathode using this. In addition, the mass ratio of the catalyst in these catalyst dispersion liquid C2 (the mass of support is included), fluorine-containing ion exchange resin, and this high molecular compound was set to mass =0.80:0.17:0.03 of the mass:book high molecular compound of mass:fluorine-containing ion exchange resin of a catalyst.

[0045] Furthermore, when thickness produced the cast film of the dimethyl silicone (KF96H -1 million) which is 80 micrometers and measured the oxygen transmission coefficient like the example

1, it was  $7.0 \times 10^{-11}$  [cm<sup>3</sup> (Normal), cm/cm<sup>2</sup>, and s-Pa].

[0046] (Example 3) 3g of the same catalyst powder as what was used for the example 1 was fed into 10g of perfluoro OKUTA decane solutions of Teflon AF 2400 used in the example 1, it agitated for 1 hour, the perfluoro OKUTA decane was further removed using the rotary evaporator, and the solid which Teflon AF 2400 was made to \*\*\*\* for a catalyst was obtained. Next, the ethanol solution of the same fluorine-containing ion exchange resin as what made this solid the electrode catalyst and used it for the example 1 was distributed, and the electrode and the film zygote were produced like the example 1 except having prepared the catalyst dispersion liquid C3 for catalyst bed formation of a cathode, and having used them instead of catalyst dispersion liquid C1. In addition, the mass ratio of the electrode catalyst in these catalyst dispersion liquid C3 and fluorine-containing ion exchange resin was set to electrode catalyst:fluorine-containing-ion-exchange-resin =0.80:0.20. In addition, the mass of this electrode catalyst shows the value with which the mass of a catalyst (the mass of support is included) and the mass of this high molecular compound (AF2400) were doubled.

[0047] (Example 4) The electrode and the film zygote were produced like the example 1 except having prepared the catalyst dispersion liquid C4 for catalyst bed formation of a cathode using the solid which Teflon AF 2400 was made to \*\*\*\* for the catalyst which prepared platinum in the example 3 instead of the catalyst of which 40 mass % support was done to the carbon black powder used when preparing the catalyst dispersion liquid C1 in an example 1.

[0048] (Example 5) The electrode and the film zygote were produced like the example 2 except having prepared the catalyst dispersion liquid C5 for catalyst bed formation of a cathode using the solid which Teflon AF 2400 was made to \*\*\*\* for the catalyst which prepared platinum in the example 3 instead of the catalyst of which 40 mass % support was done to the carbon black powder used when preparing the catalyst dispersion liquid C2 in an example 2.

[0049] (Example 1 of a comparison) The electrode and the film zygote were produced like the example 1 except having prepared the catalyst dispersion liquid C6 for catalyst bed formation of a cathode using PTFE impalpable powder (secondary particle diameter: 2 micrometers, 1 order particle diameter:0.1micrometer) as a high molecular compound which does not contain an ion exchange group instead of Teflon AF2400 used for the example 1 substantially.

[0050] Furthermore, when commercial thickness prepared the PTFE sheet which is 100 micrometers and measured the oxygen transmission coefficient like the example 1, it was  $3.0 \times 10^{-13}$  [cm<sup>3</sup> (Normal), cm/cm<sup>2</sup>, and s-Pa].

[0051] (Example 2 of a comparison) Instead of the 1 mass % perfluoro OKUTA decane solution of Teflon AF 2400 used for the example 1 The polymer (weight average molecular weight: 100,000) of CF<sub>2</sub>=CFO(CF<sub>2</sub>)<sub>2</sub> CF=CF<sub>2</sub> is prepared as a high molecular compound which does not contain an ion exchange group substantially. The mass ratio of perfluoro (2-butyl tetrahydrofuran) and perfluoro (tributylamine) dissolves this in the mixed solvent of 1:1, and the 1 mass % solution of the above-mentioned polymer is prepared. The electrode and the film zygote were produced like the example 1 except having prepared the catalyst dispersion liquid C7 for catalyst bed formation of a cathode using this.

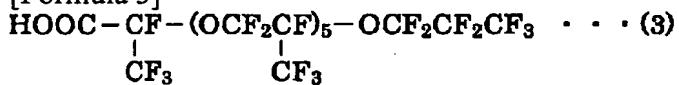
[0052] Furthermore, when thickness produced the cast film of the polymer of the polymer of CF<sub>2</sub>=CFO(CF<sub>2</sub>)<sub>2</sub> CF=CF<sub>2</sub> which is 70 micrometers and measured the oxygen transmission coefficient like the example 1, it was  $4.3 \times 10^{-13}$  [cm<sup>3</sup> (Normal), cm/cm<sup>2</sup>, and s-Pa].

[0053] (Example 3 of a comparison) The electrode and the film zygote were produced like the example 1 except having formed the catalyst bed of an anode, and the catalyst bed of a cathode using the catalyst dispersion liquid A1 in an example 1.

[0054] (Example 4 of a comparison) The fluorine-containing ether compound of the shape of an oil expressed with the following formula (3) compounded according to the example 1 of a publication to JP,11-354129,A was compounded, and this was dissolved in the ethanol solution whose concentration of fluorine-containing-ion-exchange-resin A is 5 mass % so that the mass ratio of fluorine-containing ion exchange resin and a fluorine-containing ether compound might be set to 7:3. Furthermore, to this, to carbon black powder, the catalyst which did 40 mass % support of platinum was added so that the mass ratio of a catalyst and fluorine-containing ether compound + fluorine-containing ion exchange resin might become with 0.8:0.2, and the catalyst dispersion liquid C8 for catalyst bed formation of a cathode were prepared. The electrode and the film zygote were produced

like the example 1 except having had this instead of catalyst dispersion liquid C1, and having been. [0055] Furthermore, when thickness produced the cast film of the polymer of the polymer of CF2=CFO(CF2) 2 CF=CF2 which is 70 micrometers and measured the oxygen transmission coefficient like the example 1, it was  $2.6 \times 10^{-12}$  [cm<sup>3</sup> (Normal), cm/cm<sup>2</sup>, and s-Pa].

[Formula 3]



[0056] [Cell characteristic test] It equipped with the separator with which the gas passageway was formed in each unit cell (an electrode and film zygote) of the above-mentioned example 1 - an example 5, the example 1 of a comparison - the example 3 of a comparison, and considered as the measurement cel, and the current potential characteristic test of a measurement cel was performed using an electronic load and DC power supply (the Takasago factory company make, FK400L, and EX750L). The Measuring condition was made into operating temperature; 70 degree C of hydrogen pressure force; 0.1 MPa, air pressure; 0.1 MPa, and a measurement cel, and measured the electrical potential difference between terminals of each measurement cel at the time of holding an output current consistency to 1 A/cm<sup>2</sup> with time. In addition, the electrical potential difference between terminals of each measurement cel measured the value of after [ starting ] 10 hours, 500 hours, and 1000 hours. Moreover, in this actuation condition, the hydrogen utilization factor adjusted [ the air utilization rate ] the flow rate of hydrogen gas and air as 40% 70%.

[0057]

Table 1

|       | 電池特性  |  |   |
|-------|---|--|---|
|       | 電池電圧<br>(起動後<br>10時間)<br>/mV<br>at 1A/cm <sup>2</sup> | 電池電圧<br>(起動後<br>500時間)<br>/mV<br>at 1A/cm <sup>2</sup> | 電池電圧<br>(起動後<br>1000時間)<br>/mV<br>at 1A/cm <sup>2</sup> |
| 実施例 1 | 6 6 0   | 6 5 0  | 6 5 0   |
| 実施例 2 | 6 5 0   | 6 4 0  | 6 3 0   |
| 実施例 3 | 6 6 0   | 6 6 0  | 6 5 0   |
| 実施例 4 | 6 8 0   | 6 8 0  | 6 7 0   |
| 実施例 5 | 6 7 0   | 6 6 0  | 6 5 0   |
| 比較例 1 | 4 8 0   | 4 7 0  | 4 6 0   |
| 比較例 2 | 4 9 0   | 4 9 0  | 4 8 0   |
| 比較例 3 | 5 0 0   | 4 8 0  | 4 6 0   |
| 比較例 4 | 5 3 0   | 4 8 0  | 4 6 0   |

[0058]

[Effect of the Invention] Since the overvoltage to electrode reaction can be conventionally reduced according to this invention as explained above, the polymer electrolyte fuel cell which can obtain the high cell output equipped with the gas diffusion electrode and this which have the outstanding electrode characteristic over an oxygen reduction reaction can be offered.

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[Translation done.]

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(22)Date of filing : 31.01.2001 (72)Inventor : ENDO EIJI

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(30)Priority

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**(54) GAS DIFFUSION ELECTRODE AND SOLID HIGH POLYMER TYPE FUEL CELL EQUIPPED WITH THIS**

**(57)Abstract:**

**PROBLEM TO BE SOLVED:** To provide a gas diffusion electrode having an outstanding electrode characteristic against oxygen reduction reaction, and a solid high polymer type fuel cell equipped with this, which can obtain high battery output.

**SOLUTION:** The gas diffusion electrode has a catalyst layer containing a catalyst and fluoride containing ion-exchange resin, and a gas diffusion layer arranged adjoining with the catalyst layer. A high molecular compound, which has an oxygen penetration coefficient of  $5 \times 10^{-11}$  [cm<sup>3</sup> (Normal).cm/cm<sup>2</sup>.s.Pa] or more, and does not have an ion exchange group substantially, is further contained in the catalyst layer.

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(71)出願人 000000044

旭硝子株式会社

東京都千代田区有楽町一丁目12番1号

(72)発明者 遠藤 栄治

神奈川県横浜市神奈川区羽沢町1150番地

旭硝子株式会社内

(74)代理人 100088155

弁理士 長谷川 芳樹 (外2名)

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(54)【発明の名称】 ガス拡散電極及びこれを備えた固体高分子型燃料電池

(57)【要約】

【課題】 酸素還元反応に対する優れた電極特性を有するガス拡散電極及びこれを備えた高い電池出力を得ることのできる固体高分子型燃料電池を提供する。

【解決手段】 触媒と含フッ素イオン交換樹脂とを含有する触媒層と、触媒層に隣接して配置されたガス拡散層とを備えるガス拡散電極であって、触媒層には、酸素透過係数が  $5 \times 10^{-11}$  [cm<sup>3</sup> (Normal) · cm / cm<sup>2</sup> · s · Pa] 以上であり、かつ、イオン交換基を実質的に有しない高分子化合物が更に含まれていることを特徴とする。

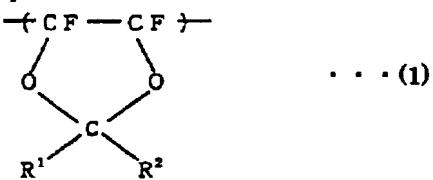
## 【特許請求の範囲】

【請求項1】触媒と含フッ素イオン交換樹脂とを含有する触媒層を備える多孔質のガス拡散電極であって、前記触媒層には、酸素透過係数が $5 \times 10^{-11}$  [cm<sup>3</sup> (Normal) · cm/cm<sup>2</sup> · s · Pa] 以上であり、かつ、イオン交換基を実質的に有しない高分子化合物が更に含まれていることを特徴とするガス拡散電極。

【請求項2】前記高分子化合物が脂肪族環構造を有するバーフルオロカーボンに基づく繰り返し単位を含む重合体であることを特徴とする請求項1に記載のガス拡散電極。

【請求項3】前記繰り返し単位が下記式(1)で表されることを特徴とする請求項2に記載のガス拡散電極。

## 【化1】



【式(1)中、R<sup>1</sup>及びR<sup>2</sup>はそれぞれ独立にフッ素原子又はトリフルオロメチル基を示す。】

【請求項4】前記高分子化合物がポリシロキサン化合物であることを特徴とする請求項1に記載のガス拡散電極。

【請求項5】前記触媒層に含まれている前記高分子化合物の含有率が前記触媒と前記含フッ素イオン交換樹脂との合量に対して0.01～30質量%であることを特徴とする請求項1～4の何れかに記載のガス拡散電極。

【請求項6】アノードと、カソードと、前記アノードと前記カソードとの間に配置された高分子電解質膜とを有する固体高分子型燃料電池であって、前記カソードとして請求項1～5の何れかに記載のガス拡散電極を備えることを特徴とする固体高分子型燃料電池。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】本発明は、ガス拡散電極及びこれを備えた固体高分子型燃料電池に関する。

## 【0002】

【従来の技術】高分子電解質膜を有する固体高分子型燃料電池は、小型軽量化が容易であることから、電気自動車等の移動車両や、小型コジェネレーションシステムの電源等としての実用化が期待されている。しかし、固体高分子型燃料電池は作動温度が比較的低くその排熱が補機動力などに有効利用しにくいため、その実用化のためにはアノード反応ガス（純水素等）の利用率及びカソード反応ガス（空気等）の利用率の高い作動条件下において、高い発電効率及び高い出力密度を得ることのできる性能が要求されている。

## 【0003】固体高分子型燃料電池のアノード及びカソ

ードの各触媒層内における電極反応は、各反応ガスと、触媒と、含フッ素イオン交換樹脂（電解質）とが同時に存在する三相界面（以下、反応サイトという）において進行する。そのため、固体高分子型燃料電池においては、従来より、金属触媒又は金属担持触媒（例えば、比表面積の大きなカーボンブラック担体に白金等の金属触媒を担持した金属担持カーボン等）等の触媒を高分子電解質膜と同種或いは異種の含フッ素イオン交換樹脂で被覆して触媒層の構成材料として使用し、いわゆる触媒層内の反応サイトの3次元化を行なうことにより当該反応サイトの増大化が図られている。

【0004】上記の触媒を被覆する含フッ素イオン交換樹脂としては、旭硝子社製「フレミオン」やデュポン社製「ナフィオン」等に代表されるようなイオン導電性が高くかつ、酸化及び還元雰囲気下において化学的に安定なスルホン酸基を有するバーフルオロカーボン重合体（以下、スルホン酸型バーフルオロカーボン重合体という）が使用されている。

【0005】しかし、従来のガス拡散電極の触媒層に含まれている含フッ素イオン交換樹脂はイオン伝導性と化学的安定性に優れている反面、樹脂内のガス透過性が不十分であるため、特にガス拡散電極をカソードとして使用する場合、触媒層内の酸素透過性が不十分となり、カソードにおける酸素還元反応の過電圧が大きくなり、高い電極特性を得ることが困難となっていた。

【0006】これに対して、特開平11-354129号公報においては、触媒を被覆する含フッ素イオン交換樹脂に含フッ素エーテル化合物を混合してカソードの触媒層内の酸素透過性を増加させることによりカソードの過電圧の低減を図った固体高分子形燃料電池が提案されている。

## 【0007】

【発明が解決しようとする課題】しかしながら、本発明者らは、特開平11-354129号公報に記載の固体高分子形燃料電池であっても、カソードの触媒層内の酸素透過性が不十分であり、カソードの過電圧を十分に低減できておらず、また、カソードの触媒層の耐久性が不十分であり、電池寿命が短いという問題があることを見出した。これは、好ましいとされる含フッ素エーテル化合物が油状の低分子化合物であるため、発電中においてこれが反応生成水に徐々に溶解するか、それに同伴して含フッ素イオン交換樹脂から脱離し、更に、生成水とともに触媒層から排出されてしまうからであると考えられる。

【0008】本発明は、上記従来技術の有する課題に鑑みてなされたものであり、酸素還元反応に対する優れた電極特性を有するガス拡散電極及びこれを備えた高い電池出力を得ることのできる固体高分子型燃料電池を提供することを目的とする。

## 【0009】

【課題を解決するための手段】本発明者らは、上記目的を達成するべく鋭意研究を重ねた結果、高い酸素透過性を有しかつ実質的にイオン交換基を有しない高分子化合物をカソードの触媒層に含有させることにより、カソードにおける電極特性を向上させることができることを見出し、本発明に到達した。

【0010】そこで、本発明は、触媒と含フッ素イオン交換樹脂とを含有する触媒層を備える多孔質のガス拡散電極であって、触媒層には、酸素透過係数が $5 \times 10^{-11}$  [cm<sup>3</sup> (Normal) · cm/cm<sup>2</sup> · s · Pa] 以上であり、かつ、イオン交換基を実質的に有しない高分子化合物が更に含まれていることを特徴とするガス拡散電極を提供する。

【0011】本発明のガス拡散電極は、上記の酸素透過係数を有する高分子化合物（以下、本高分子化合物という）が触媒層に含有されているので、触媒層内の反応サイト近傍の反応ガスの濃度を従来よりも高くすることができる。その結果、電極反応における交換電流密度を増大させることができ、酸素過電圧を低減できる。すなわち、高い電極特性を得ることができる。特に、このガス拡散電極を固体高分子型燃料電池のカソードとして使用すれば、カソードの酸素還元反応の過電圧を効果的に低減させることができるので、カソードの電極特性を向上させることができる。

【0012】また、触媒層内に含有される本高分子化合物は撥水化剤としても機能するので、触媒層内のガス拡散に寄与している細孔に加湿用水や反応生成水が滞留し、細孔が閉塞されてしまうラッディングの発生を効果的に防止することができる。更に、本発明における本高分子化合物は水、アルコール等の水性溶媒に対して実質的に不溶であるので、長期作動中において触媒近傍から脱離し、触媒層から排出されてしまうといった不具合の発生を十分に防止することができる。その結果、本発明のガス拡散電極は高い電極特性を長期にわたり安定して得ることが可能となる。

【0013】ここで、酸素透過係数が $5 \times 10^{-11}$  [cm<sup>3</sup> (Normal) · cm/cm<sup>2</sup> · s · Pa] 未満であると、触媒層内の反応サイト近傍の反応ガスの濃度を十分に高くすることが困難となり、酸素電極反応の過電圧を十分に低減することが困難となる。また、上記と同様の観点から、本発明における本高分子化合物の酸素透過係数は、 $6 \times 10^{-11}$  [cm<sup>3</sup> (Normal) · cm/cm<sup>2</sup> · s · Pa] 以上であることが好ましい。

【0014】なお、本発明における本高分子化合物の酸素透過係数とは、本高分子化合物から作製したキャスト膜を理化精機工業社製の分離膜素材ガス透過測定装置にセットし、高真空法に基づいて測定された25°C、10<sup>1</sup> Paにおけるキャスト膜の酸素透過係数を示す。

【0015】更に、本発明における「イオン交換基を実質的に有しない本高分子化合物」とは、分子中のイオン

交換容量（以下、A<sub>i</sub>という）が0.10ミリ当量/g乾燥樹脂（以下、meq./gとする）以下である高分子化合物を示す。このような本高分子化合物は、水、アルコール等の水性溶媒に対して実質的に不溶であるので、前述のように長期作動中において触媒近傍から脱離し、触媒層から排出されてしまうといった不具合の発生を十分に防止することができる。また、この本高分子化合物のA<sub>i</sub>は、同様の観点から、0.05 meq./g以下であることが好ましい。更に、ここでいうイオン交換基とは、具体的にはスルホン酸基、カルボン酸基等である。

【0016】また、本発明は、アノードと、カソードと、アノードとカソードとの間に配置された高分子電解質膜とを有する固体高分子型燃料電池であって、カソードとして前述の本発明のガス拡散電極を備えることを特徴とする固体高分子型燃料電池を提供する。

【0017】このように、先に述べた酸素還元反応に対する優れた電極特性を有する本発明のガス拡散電極をカソードとして備えることにより、高い電池出力を有する固体高分子型燃料電池を構成することが可能となる。また、先に述べたように、本発明のガス拡散電極はラッディングの発生を十分に防止することができるとともに耐久性に優れているので、これを備える本発明の固体高分子型燃料電池は高い電池出力を長期にわたり安定して得ることが可能となる。

【0018】

【発明の実施の形態】以下、本発明のガス拡散電極及びこれを備えた固体高分子型燃料電池の好適な実施形態について詳細に説明する。

【0019】本実施形態の固体高分子型燃料電池のガス拡散電極であるカソード及びアノードは、触媒層を備えるが、何れも触媒層と、該触媒層に隣接して配置されるガス拡散層とからなることが好ましい。ガス拡散層の構成材料としては、例えば、電子伝導性を有する多孔質体（例えば、カーボンクロスやカーボンペーパー）が使用される。

【0020】カソードの触媒層には、主として含フッ素イオン交換樹脂と、この含フッ素イオン交換樹脂により被覆された触媒と、先に述べた酸素透過係数が $5 \times 10^{-11}$  [cm<sup>3</sup> (Normal) · cm/cm<sup>2</sup> · s · Pa] 以上であり、かつ、イオン交換基を実質的に有しない本高分子化合物とが含有されており、カソードにおける酸素還元反応に対する過電圧を低減させることによるカソードの電極反応速度の向上が図られている。

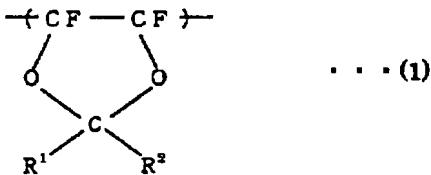
【0021】ここで、水、アルコール等の水性溶媒に対して実質的に不溶とするという観点から、本高分子化合物の重量平均分子量は、1000～3000000であることが好ましく、20000～1000000であることがより好ましい。本高分子化合物の重量平均分子量が1000未満であると、長期の発電において電極から

脱落する可能性がある。一方、本高分子化合物の重量平均分子量が30000000を超えると、溶媒に溶解しにくくなり、電極作製の際に作製法が限られてしまう。

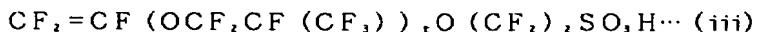
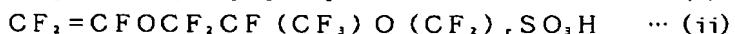
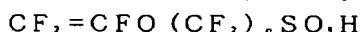
【0022】また、本高分子化合物は、脂肪族環構造を有するバーフルオロカーボンに基づく繰り返し単位を含む重合体であることが好ましい。分子内に脂肪族環構造を有するバーフルオロカーボンに基づく繰り返し単位を含む重合体は、その分子構造に起因する分子のねじれにより結晶化しにくく、酸素透過性が高い。また、この重合体は、フッ素系溶剤に可溶であり、耐薬品性に優れ、酸化・還元雰囲気でも安定なので好ましい。

【0023】上記の脂肪族環構造を有するバーフルオロカーボンに基づく繰り返し単位としては、下記式(1)で表される繰り返し単位が好ましい。ここで、下記式(1)中、R<sup>1</sup>及びR<sup>2</sup>はそれぞれ独立にフッ素原子又はトリフルオロメチル基を示す。このような分子構造を有する化合物としては、商品名としては例えば、「テフロン(登録商標) AF 2400」(酸素透過係数: 1.2 × 10<sup>-10</sup> [cm<sup>3</sup> (Normal) · cm/cm<sup>2</sup> · s · Pa])等が挙げられる。

【化2】



【0024】また、本高分子化合物として上記の重合体と異なる構造を有する化合物を挙げると、本発明の本高分子化合物はポリシロキサン化合物であることが好ましい。ポリシロキサン化合物は、高い酸素透過性を有するので好ましい。ポリシロキサン化合物の中でも、高い酸素透過係数 (6.95 × 10<sup>-11</sup> [cm<sup>3</sup> (Normal) · cm/cm<sup>2</sup> · s · Pa]) を有しているという観点から、下記式(2)で表される構造の繰り返し単位を有するポリジメチルシロキサンがより好ましい。ここで、式(2)中、nは14～4×10<sup>4</sup>の整数を示す。\*



【0029】なお、上記共重合体には、ヘキサフルオロプロピレン等の含フッ素オレフィン又はバーフルオロ(アルキルビニルエーテル)に基づく繰り返し単位が、テトラフルオロエチレンに基づく繰り返し単位の25質量%以下であればテトラフルオロエチレンに基づく繰り返し単位と置き換わって含まれていてもよい。

【0030】また、本発明のガス拡散電極の触媒層に含有される含フッ素イオン交換樹脂のA<sub>n</sub>は、0.3～1.5 meq./g であることが好ましい。含フッ素イオン交換樹脂のA<sub>n</sub>が0.3 meq./g未満となる

\* - (O-Si(CH<sub>3</sub>)<sub>2</sub>)<sub>n</sub> - … (2)

【0025】また、触媒層に含まれている本高分子化合物の含有率は触媒と含フッ素イオン交換樹脂との合量に対して0.01～30質量%であることが好ましく、0.01～20質量%であることがより好ましい。ここで、本高分子化合物の含有率が0.01質量%未満であると、酸素還元反応に対する酸素過電圧を十分に低減することが困難となる傾向が大きくなる。一方、本高分子化合物の含有率が30質量%を超えると触媒層中に含有される含フッ素イオン交換樹脂の含有率が相対的に低下し、その結果、触媒層中に含有される触媒に対する含フッ素イオン交換樹脂の被覆率が低下して有効に機能する反応サイトが減少するため高い電極特性を得ることが困難となる傾向が大きくなる。

【0026】更に、本発明のガス拡散電極の触媒層に含まれる触媒は特に限定されるものではないが、白金又は白金合金が好ましい。更に、触媒層中に含有される触媒は、電気伝導性の担体に担持されていることが好ましい。この担体は特に限定されないが、比表面積が200 m<sup>2</sup>/g以上のカーボン材料が好ましい。例えば、カーボンブラックや活性炭などが好ましく使用される。

【0027】また、本発明のガス拡散電極の触媒層に含有される含フッ素イオン交換樹脂は、スルホン酸型バーフルオロカーボン重合体であることが好ましい。スルホン酸型バーフルオロカーボン重合体は、触媒層内において長期間化学的に安定でかつ速やかなプロトン伝導を可能にする。

【0028】更に、スルホン酸型バーフルオロカーボン重合体は、CF<sub>2</sub>=CF-(OCF<sub>2</sub>CFX)<sub>m</sub>-O-(CF<sub>2</sub>)<sub>n</sub>-SO<sub>3</sub>Hで表されるフルオロビニル化合物に基づく繰り返し単位(式中、mは0～3の整数、nは1～12の整数、pは0又は1であり、XはF又はCF<sub>2</sub>である)とテトラフルオロエチレンに基づく繰り返し単位とからなる共重合体が好ましい。上記フルオロビニル化合物の好ましい例としては、以下(i)～(iii)の化合物が挙げられる。ただし、下記式中、qは1～8の整数、rは1～8の整数、tは1～3の整数を示す。

… (i)

… (ii)

… (iii)

と、反応サイトが著しく減少するため十分な電池出力を得ることが困難になる傾向がある。一方、含フッ素イオン交換樹脂のA<sub>n</sub>が1.5 meq./gを超えると、含フッ素イオン交換樹脂中のイオン交換基の密度が増大し、触媒層におけるガス拡散性或いは排水性が低下してフラッディングが発生し易くなる。触媒層に含有されている含フッ素イオン交換樹脂のA<sub>n</sub>は、上記と同様の観点から、0.5～1.5 meq./gであることがより好ましい。

【0031】また、本発明のガス拡散電極の触媒層の層

厚は、通常のガス拡散電極と同等であればよく、1～100  $\mu\text{m}$  あることが好ましく、3～50  $\mu\text{m}$  あることがより好ましい。

【0032】固体高分子型燃料電池においては、通常、アノードの水素酸化反応の過電圧に比較してカソードの酸素還元反応の過電圧が非常に大きいので、上記のようにカソードの触媒層内の反応サイト近傍の酸素濃度を増加させて当該反応サイトを有効に利用し、カソードの電極特性を向上させることは、電池の出力特性を向上させる上で効果的である。

【0033】一方、アノードの構成は特に限定されず、例えば、公知のガス拡散電極の構成を有していてもよいが、上記のカソードと同様の構造を有するように構成することが好ましい。これによりカソードに加えてアノードの電極特性も向上させることができるとなり、電池出力をより向上させ、かつ、長期にわたる作動を行う場合もその高い電池出力を保持することをより確実に図ることができる。

【0034】また、本発明の固体高分子型燃料電池に使用する高分子電解質膜は、湿潤状態で良好なイオン伝導性を示すイオン交換膜であれば特に限定されない。高分子電解質膜を構成する固体高分子材料としては、例えば、スルホン酸基を有するバーフルオロカーボン重合体、ポリサルホン樹脂、ホスホン酸基又はカルボン酸基を有するバーフルオロカーボン重合体等を用いることができる。中でも、スルホン酸型バーフルオロカーボン重合体が好ましい。そして、この高分子電解質膜は、触媒層に含まれる含フッ素イオン交換樹脂と同じ樹脂からなっていてもよく、異なる樹脂からなっていてもよい。

【0035】本発明のガス拡散電極は、含フッ素イオン交換樹脂と触媒と本高分子化合物とが溶媒又は分散媒に溶解又は分散した塗工液を用いて作製することが好ましい。ここで用いる溶媒又は分散媒としては、例えばアルコール、含フッ素アルコール、含フッ素エーテル等が使用できる。そして、塗工液をイオン交換膜又はガス拡散層となるカーボンクロス等に塗工することにより触媒層が形成される。また、別途用意した基材に上記塗工液を塗工して塗工層を形成し、これをイオン交換膜上に転写することによってもイオン交換膜上に触媒層が形成できる。

【0036】ここで、触媒層をガス拡散層上に形成した場合には、触媒層とイオン交換膜とを接着法（特開平7-220741、特開平7-254420）やホットプレス等により接合することが好ましい。また、イオン交換膜上に触媒層を形成した場合には、触媒層のみでガス拡散電極を構成してもよいが、更に触媒層に隣接してガス拡散層を配置し、ガス拡散電極としてもよい。

【0037】ガス拡散電極の外側には、通常ガスの流路が形成されたセパレータが配置され、当該流路にアノードには水素を含むガス、カソードには酸素を含むガスが

供給されて固体高分子型燃料電池が構成される。

【0038】

【実施例】以下、実施例及び比較例を挙げて本発明のガス拡散電極及び固体高分子型燃料電池について詳しく説明するが、本発明はこれらの実施例に限定されるものではない。

【0039】（実施例1）実施例1の単位セルは、以下に説明する手順により作製した。触媒は、カーボンブラック粉末に白金を40質量%担持したものを用いた。含

10 フッ素イオン交換樹脂としては、テトラフルオロエチレンに基づく繰り返し単位と  $\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_3\text{H}$  に基づく繰り返し単位とからなる共重合体からなる含フッ素イオン交換樹脂（ $A_n=0.91\text{ meq.}/\text{g}$ 、以下、含フッ素イオン交換樹脂Aという）を用い、エタノールに溶解させてこの含フッ素イオン交換樹脂の濃度が5質量%であるエタノール溶液を調製した。また、本高分子化合物としてデュポン社製の商品名「テフロンAF2400」を用意し、これをバーフルオロオクタデカンに溶解させてこのテフロンAF2400の濃度が1質量%であるバーフルオロオクタデカン溶液を調製した。次に、上記のエタノール溶液、バーフルオロオクタデカン溶液及び触媒を混合し、カソードの触媒層形成用の触媒分散液C1を調製した。なお、この触媒分散液C1中の触媒（担体の質量を含む）、含フッ素イオン交換樹脂及び本高分子化合物の質量比は、触媒の質量：含フッ素イオン交換樹脂の質量：本高分子化合物の質量=0.8：0.15：0.05とした。

30 30 【0040】また、上記含フッ素イオン交換樹脂Aをエタノールに溶解させて、エタノール溶液を調製した。次に、触媒分散液C1で用いたものと同じ触媒の粉末を上記エタノール溶液中に添加して十分に混合し、アノードの触媒層形成用の触媒分散液A1を調製した。なお、この触媒分散液A1中の触媒（担体の質量を含む）及び含フッ素イオン交換樹脂の質量比は、触媒の質量：含フッ素イオン交換樹脂の質量=0.8：0.2とした。

40 40 【0041】次に、ガス拡散層として、撥水性カーボンクロス（繊維織布）を撥水性カーボン粉末層（カーボンブラックとPTFEの混合物）で目詰めした厚さ300  $\mu\text{m}$  のものを用意した。また、高分子電解質膜として、スルホン酸型バーフルオロカーボン重合体からなるイオン交換膜（商品名：フレミオンS、旭硝子社製、 $A_n=1.0\text{ meq.}/\text{g}$ 、乾燥膜厚80  $\mu\text{m}$ ）を用意した。

【0042】次に、カソードの触媒層の白金の含有量が0.5mg/cm<sup>2</sup>となるように触媒分散液1を上記高分子電解質膜の一方の面に噴霧した。また、アノードの触媒層の白金の含有量が0.5mg/cm<sup>2</sup>となるように触媒分散液A1を上記高分子電解質膜のもう一方の面に噴霧した。次に、上記の触媒分散液C1と触媒分散液A1とを噴霧した高分子電解質膜を大気中、100°Cで

1時間乾燥させた。

【0043】また、上記のテフロンAF2400の濃度が5質量%であるバーフルオロオクタデカン溶液をシャーレに流し込み、その後溶媒を除去して厚さが90μmのテフロンAF2400のキャスト膜を作製した。更に、上記の含フッ素イオン交換樹脂の濃度が5質量%であるエタノール溶液をシャーレに流し込み、厚さが90μmの含フッ素イオン交換樹脂のキャスト膜を作製した。そして、理化精機工業社製の分離膜素材ガス透過測定装置を用いて先に述べた条件及び方法によりテフロンAF2400のキャスト膜と含フッ素イオン交換樹脂のキャスト膜との酸素透過係数を測定した。その結果、テフロンAF2400のキャスト膜の酸素透過係数は $1.2 \times 10^{-10}$  [cm<sup>3</sup> (Normal) · cm/cm<sup>2</sup> · s · Pa] であり、含フッ素イオン交換樹脂のキャスト膜の酸素透過係数は $4.8 \times 10^{-12}$  [cm<sup>3</sup> (Normal) · cm/cm<sup>2</sup> · s · Pa] であった。

【0044】(実施例2) 実施例1において調製したテフロンAF2400のバーフルオロオクタデカン溶液のかわりに、本高分子化合物として信越化学工業社製の商品名「ジメチルシリコーン(KF96H-100万)」をトルエンに溶解させてその濃度が5質量%であるトルエン溶液を調製し、これを用いた以外は実施例1と同様にして触媒分散液C2を調製し、これを用いてカソードを作製した以外は実施例1と同様にして電極・膜接合体を作製した。なお、この触媒分散液C2中の触媒(担体の質量を含む)、含フッ素イオン交換樹脂及び本高分子化合物の質量比は、触媒の質量：含フッ素イオン交換樹脂の質量：本高分子化合物の質量=0.80:0.17:0.03とした。

【0045】更に、厚さが80μmのジメチルシリコーン(KF96H-100万)のキャスト膜を作製し、実施例1と同様にしてその酸素透過係数を測定したところ $7.0 \times 10^{-11}$  [cm<sup>3</sup> (Normal) · cm/cm<sup>2</sup> · s · Pa] であった。

【0046】(実施例3) 実施例1で用いたテフロンAF2400のバーフルオロオクタデカン溶液10gに実施例1に用いたものと同様の触媒粉末3gを投入して1時間攪拌し、更にロータリーエバボレータを用いてバーフルオロオクタデカンを除去し、触媒にテフロンAF2400を含侵させた固形物を得た。次に、この固形物を電極触媒とし実施例1に用いたものと同様の含フッ素イオン交換樹脂のエタノール溶液に分散させ、カソードの触媒層形成用の触媒分散液C3を調製し触媒分散液C1のかわりに用いた以外は実施例1と同様にして電極・膜接合体を作製した。なお、この触媒分散液C3中の電極触媒と含フッ素イオン交換樹脂との質量比は、電極触媒：含フッ素イオン交換樹脂=0.80:0.20とした。なお、この電極触媒の質量は、触媒(担体の質量を含む)の質量と本高分子化合物(AF2400)の質量

とを合わせた値を示す。

【0047】(実施例4) 実施例1における触媒分散液C1を調製する際に使用したカーボンブラック粉末に白金を40質量%担持した触媒のかわりに実施例3において調製した触媒にテフロンAF2400を含侵させた固形物を使用してカソードの触媒層形成用の触媒分散液C4を調製した以外は、実施例1と同様にして電極・膜接合体を作製した。

【0048】(実施例5) 実施例2における触媒分散液C2を調製する際に使用したカーボンブラック粉末に白金を40質量%担持した触媒のかわりに実施例3において調製した触媒にテフロンAF2400を含侵させた固形物を使用してカソードの触媒層形成用の触媒分散液C5を調製した以外は、実施例2と同様にして電極・膜接合体を作製した。

【0049】(比較例1) 実施例1に用いたテフロンAF2400のかわりに、イオン交換基を実質的に含まない高分子化合物としてPTFE微粉末(2次粒子径: 2μm、1次粒子径: 0.1μm)を使用しカソードの触媒層形成用の触媒分散液C6を調製した以外は実施例1と同様にして電極・膜接合体を作製した。

【0050】更に、市販の厚さが100μmのPTFEシートを用意し、実施例1と同様にしてその酸素透過係数を測定したところ、 $3.0 \times 10^{-13}$  [cm<sup>3</sup> (Normal) · cm/cm<sup>2</sup> · s · Pa] であった。

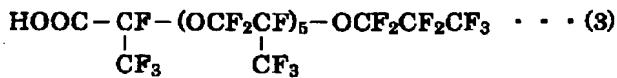
【0051】(比較例2) 実施例1に用いたテフロンAF2400の1質量%バーフルオロオクタデカン溶液のかわりに、イオン交換基を実質的に含まない高分子化合物としてCF<sub>2</sub>=CFO(CF<sub>2</sub>)<sub>2</sub>CF=CF<sub>2</sub>の重合体(重量平均分子量: 10万)を用意し、これをバーフルオロ(2-ブチルテトラヒドロフラン)とバーフルオロ(トリブチルアミン)との質量比が1:1の混合溶媒に溶解させて上記重合体の1質量%溶液を調製し、これを用いてカソードの触媒層形成用の触媒分散液C7を調製した以外は実施例1と同様にして電極・膜接合体を作製した。

【0052】更に、厚さが70μmのCF<sub>2</sub>=CFO(CF<sub>2</sub>)<sub>2</sub>CF=CF<sub>2</sub>の重合体の重合体のキャスト膜を作製し、実施例1と同様にしてその酸素透過係数を測定したところ、 $4.3 \times 10^{-13}$  [cm<sup>3</sup> (Normal) · cm/cm<sup>2</sup> · s · Pa] であった。

【0053】(比較例3) 実施例1における触媒分散液A1を用いてアノードの触媒層とカソードの触媒層を形成した以外は実施例1と同様にして電極・膜接合体を作製した。

【0054】(比較例4) 特開平11-354129号公報に記載の実施例1に従って合成した下記式(3)で表される油状の含フッ素エーテル化合物を合成し、これを含フッ素イオン交換樹脂Aの濃度が5質量%であるエタノール溶液に、含フッ素イオン交換樹脂と含フッ素エ

一テル化合物との質量比が7:3となるように溶解させた。更に、これに、カーボンブラック粉末に白金を40質量%担持した触媒を、触媒と含フッ素エーテル化合物+含フッ素イオン交換樹脂との質量比が0.8:0.2となるように添加してカソードの触媒層形成用の触媒分散液C8を調製した。これを触媒分散液C1のかわりにもちいた以外は実施例1と同様にして電極・膜接合体を\*



【0056】[電池特性試験]上記の実施例1～実施例5、比較例1～比較例3の各単位セル(電極・膜接合体)にガス流路の形成されたセパレータを装着して測定セルとし、電子負荷と直流電源(高砂製作所社製、FK400L及びEX750L)を用いて測定セルの電流電圧特性試験を行った。測定条件は、水素圧力:0.1MPa、空気圧力:0.1MPa、測定セルの作動温度:70°Cとし、出力電流密度を1A/cm<sup>2</sup>に保持した場※

\*作製した。

【0055】更に、厚さが70μmのCF<sub>2</sub>=CFO(CF<sub>2</sub>)<sub>2</sub>CF=CF<sub>2</sub>の重合体の重合体のキャスト膜を作製し、実施例1と同様にしてその酸素透過係数を測定したところ、 $2.6 \times 10^{-12} [\text{cm}^3 (\text{Normal}) \cdot \text{cm} / \text{cm}^2 \cdot \text{s} \cdot \text{Pa}]$ であった。

【化3】

※合における各測定セルの端子間電圧を経時的に測定した。なお、各測定セルの端子間電圧は、起動後10時間、500時間及び1000時間の値を測定した。また、この作動条件において水素利用率が70%、空気利用率が40%となにより水素ガス及び空気の流量を調節した。

【0057】

【表1】

|      | 電池特性  |  |   |
|------|---|--|---|
|      | 電池電圧<br>(起動後<br>10時間)<br>/mV<br>at 1A/cm <sup>2</sup> | 電池電圧<br>(起動後<br>500時間)<br>/mV<br>at 1A/cm <sup>2</sup> | 電池電圧<br>(起動後<br>1000時間)<br>/mV<br>at 1A/cm <sup>2</sup> |
| 実施例1 | 660   | 650  | 650   |
| 実施例2 | 650   | 640  | 630   |
| 実施例3 | 660   | 660  | 650   |
| 実施例4 | 680   | 680  | 670   |
| 実施例5 | 670   | 660  | 650   |
| 比較例1 | 480   | 470  | 460   |
| 比較例2 | 490   | 490  | 480   |
| 比較例3 | 500   | 480  | 460   |
| 比較例4 | 530   | 480  | 460   |

【0058】

【発明の効果】以上説明したように、本発明によれば、電極反応に対する過電圧を従来よりも低減させることができるので、酸素還元反応に対する優れた電極特性を有

30 するガス拡散電極及びこれを備えた高い電池出力を得ることのできる固体高分子型燃料電池を提供することができる。